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RESEARCH MEMORANDUM

VAPOR PRESSURES AND CALCULATED HEATS OF VAPORIZATION OF CONCENTRATED NITRIC ACID SOLUTIONS IN THE COMPOSITION RANGE 71 TO 89 PERCENT NITRIC ACID, 7 TO 20 PERCENT NITROGEN DIOXIDE, 1 TO 10 PERCENT WATER, AND IN THE TEMPERATURE RANGE 10° TO 60° C

By A. B. McKeown and Frank E. Belles

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VAPOR PRESSURES AND CALCULATED HEATS OF VAPORIZATION OF CONCENTRATED NITRIC ACID SOLUTIONS IN THE COMPOSITION RANGE 71 TO 89 PERCENT NITRIC ACID, 7 TO 20 PERCENT NITROGEN DIOXIDE, 1 TO 10 PERCENT WATER, AND IN THE TEMPERATURE RANGE 10° TO 60° C

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SUMMARY

Total vapor pressures were measured for 16 acid mixtures of the ternary system nitric acid, nitrogen dioxide, and water within the temperature range 10° to 60° C and within the composition range 71 to 89 weight percent nitric acid, 7 to 20 weight percent nitrogen dioxide, and 1 to 10 weight percent water. Heats of vaporization were calculated from the vapor pressure measurements for each sample for the temperatures, 25°, 40°, and 60° C. The ullage of the apparatus used for the measurements was 0.46.

Ternary diagrams showing isobars as a function of composition of the system were constructed from experimental and interpolated data for the temperatures 25°, 40°, 45°, and 60° C and are presented herein.

INTRODUCTION

Concentrated solutions of nitric acid containing oxides of nitrogen are commonly used in many propellant and chemical applications. Certain properties such as vapor pressures and heats of vaporization are therefore of considerable interest. As pointed out in reference 1, the data reported in the literature on the vapor pressures of the system nitric acid, nitrogen dioxide, and water are incomplete with respect to the composition range of interest.

Vapor pressures of nitric acid solutions have been measured in the composition range 83 to 97 percent nitric acid, 0 to 6 percent nitrogen dioxide, and 0 to 15 percent water, for the temperature range 20° to 80° C

(ref. 1). This is only a part of the composition range of interest. The total vapor pressures of 16 mixtures of nitric acid, water, and nitrogen dioxide were therefore determined by use of an isoteniscope for the composition range 71 to 89 weight percent nitric acid, 7 to 20 weight percent nitrogen dioxide, and 0 to 10 weight percent water.

APPARATUS

A diagrammatic sketch of the equipment is shown in figure 1. The apparatus consisted of an isoteniscope, a mercury manometer, a thermometer, a vacuum system, and a heat-control unit.

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Isoteniscope. - A Smith and Menzies type isoteniscope, made of pyrex and modified by the addition of a reservoir to contain the separating fluid during the degasification procedure, was used to obtain the vapor pressure measurements. The instrument was essentially of the same design as that of reference 1 except that a small-bore U-tube, of 4-millimeter inside diameter, was used in order to yield a small area of contact between the separating fluid (Fluorolube S) and the acid vapors. The acid chamber was filled with approximately 5 milliliters of acid during the operation of the apparatus. Ground-glass joints were lubricated with Halocarbon stopcock grease, which resisted attack by the acids. The ullage of the isoteniscope, that is, the ratio of the vapor volume to vapor volume plus liquid volume, was approximately 0.46 under operating conditions.

Temperature control system. - The isoteniscope was maintained at specified temperatures by immersion in a 4000-milliliter transparent Dewar flask filled with water at a predetermined temperature. The water was heated in a separate constant-temperature bath and was circulated through the Dewar flask by a pump during experimental runs. The constant-temperature bath was heated by two 750-watt immersion-type heaters connected in series with an immersion-type thermoswitch, which controlled the temperature of the bath to $\pm 0.5^{\circ}$ C. The temperature of the liquid in the Dewar flask was measured by a calibrated thermometer that could be read to $\pm 0.2^{\circ}$ C.

PROCEDURE

Preparation of acid samples. - Acid samples were prepared by mixing aliquot portions of 99.6 percent HNO_3, distilled H_2O, and 33.5 percent by weight solution of NO_2 in HNO_3. The 99.6 percent HNO_3 was prepared by the vacuum distillation of a mixture comprising two parts of concentrated sulfuric acid and three parts of commercial white fuming nitric acid (approximately 98 percent HNO_3) at a temperature of 10° to 15° C. The 33.5 percent solution of NO_2 in HNO_3 was prepared by passing gaseous NO_2 into 99.6 percent HNO_3.

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Degasification of acid sample. - Acid samples were degassed in the isoteniscope by the method discussed in reference 1 to remove absorbed carbon dioxide and air. In order to avoid the possibility of carbon dioxide being retained in the acid sample in the frozen state, an ethanol-water solution at a temperature of -95° to -100° C was used as a cooling medium in the final repetition of the degasification procedure.

Measurement of vapor pressures. - Following degasification, vapor pressures of the acid mixtures were determined by the procedure described in reference 1 for the temperature range 10° C to the normal boiling point. Pressure measurements were made at successively higher temperatures; and after the pressure reading at the highest temperature was taken, the acid sample was cooled to one of the lower temperatures and another reading was taken. The purpose of this reading was to detect any pressure changes that might have occurred during the run due to decomposition of the acid or absorption of the acid vapors in the Fluorolube S.

Pressure measurements were made at all temperatures within the time interval 30 to 40 minutes.

Acid analysis. - The acid samples were analyzed by the method of U. S. Air Force Specification No. 14104 with the exception that total acidity was determined by direct titration of the acid sample in water with NaOH solution. In accordance with the specification, the NO_2 was determined by back-titration of the sample in $Ce(NH_4)_2(SO_4)_3$ solution with $FeSO_4$. Water content was determined by the subtraction of the sum of the NO_2 content and HNO_3 content from 100 percent.

Acid analyses were made on both stock solutions and on samples taken from the isoteniscope after experimental runs. The acid analyses reported in table I are for stock solutions, inasmuch as fresh samples from stock solutions were used for each experimental run. The analyses in table I represent the average of two determinations for each sample.

RELIABILITY OF MEASUREMENTS

Accuracy of apparatus. - The inherent accuracy of the apparatus was checked by comparison of the measured vapor pressures of distilled water with the values reported in the literature. The experimental data and the literature values for the same temperature are presented in the following table:

Temperature, °C	Vapor pressure, mm Hg		Deviation, percent
	Experimental	Literature[a]	
14.2	11.8	12.1	-2.5
20.0	17.8	17.5	1.7
32.0	35.7	35.7	0.0
43.0	65.0	64.8	.3
52.3	104.0	103.6	.4
62.0	163.4	163.8	-.2
78.8	333.1	338.3	-1.5

[a]Values for water from ref. 2 (table 9, p. 391).

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From this table it appears that the experimental error associated with this apparatus is of the order of 1 to 1.5 percent.

Ullage effects. - The ullage of the isoteniscope in this investigation was approximately 0.46 under operating conditions. For several samples the ullage was varied approximately 10 percent between the first run and the check run without measurable change in the vapor pressure.

For the ranges of composition, temperature, and vapor pressure covered in this investigation, a change of ullage from zero to as large as 0.75 would cause a change of less than one half of one percent in the concentration of NO_2 in the liquid phase. Significant errors in the information would be introduced by direct, uncorrected application of these data to systems with very large ullage, such as 0.95 or greater.

Effects of decomposition, absorption, and degasification. - As described earlier, the vapor pressure of each sample was measured twice at one of the lower temperatures, once at the beginning of the run and once at the conclusion. For most of the samples the second pressure was slightly higher than the initial measurement, indicating that a certain amount of decomposition had probably taken place during the run. For a few of the samples the second pressure was slightly less than the initial pressure, which may have been due to minor absorption of acid vapors by the Fluorolube S at the area of contact. The largest pressure increase experienced for all the experimental runs was 8.0 millimeters of mercury and the average increase for all experimental runs was 1.6 millimeters of mercury. The largest pressure decrease for all the experimental runs was 2.0 millimeters of mercury.

Further evidence, given by the following table, shows that change in composition of the acid due to decomposition, absorption, and degasification is small. The data in this table were obtained by analysis of three acid samples both before and after experimental runs.

Sample	Analysis, percent by weight			
		HNO_3	NO_2	H_2O
4	Stock solution	86.21	10.40	3.39
	After experimental run 2	86.10	10.31	3.59
11	Stock solution	81.42	16.79	1.79
	After experimental run 2	81.25	16.80	1.95
1	Stock solution	88.42	7.82	3.76
	After experimental run 2	88.17	7.91	3.92

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RESULTS AND DISCUSSION

The measured vapor pressures of 16 acid mixtures are presented in table I. Vapor pressures were not measured at temperatures above normal boiling points since limiting features of the apparatus made it impossible to measure vapor pressures above 1 atmosphere.

Figure 2 is a logarithmic plot of total vapor pressure of the acid against vapor pressure of water (ref. 2) at equal temperature (methods from refs. 3 and 4). This figure is a plot of the raw data for all the acid samples. No significance is attached to the way the samples are grouped. When great accuracy is not needed, the vapor pressures of the various acids above their normal boiling points may be obtained by extrapolation of the curves in this figure.

Figure 3 is presented to show the effect of variation of composition of the acid sample on vapor pressure at temperatures of 25°, 40°, and 45° C. An attempt was made to prepare samples in sets of approximately constant NO_2 concentration for the purpose of relating composition of the acid with vapor pressure at specific temperatures. The concentrations were 7.62-7.82, 10.11-10.40, 13.35-13.58, 16.66-16.79, and 19.27-19.37 percent NO_2 with varying amounts of HNO_3 and H_2O. In figure 3 vapor pressure is plotted against weight percent H_2O for the NO_2 concentrations mentioned. Vapor-pressure values were obtained from the smooth curves of the pressure-temperature data of table I for each acid composition. These data indicate that, within the composition range studied, an increase in total vapor pressure is produced by an increase in H_2O content for constant NO_2 content. It has been found that this relation is applicable for acids containing approximately 2 percent NO_2 or more (ref. 1).

Ternary diagrams showing isobars as a function of the composition of the system NO_2-H_2O-HNO_3 were constructed from interpolated and experimental data taken from figure 3 and are presented in figure 4.

Figures 4(a), (b), and (d) include both the data of reference 1 and the present data. These diagrams, while subject to small inaccuracies due to the method of their construction, may be used to estimate the vapor pressure, at 25°, 40°, 45°, and 60° C, of any sample within the range of composition covered by the ternary plot. Estimates at two different temperatures may then be used to obtain a straight-line plot similar to figure 1 (method from refs. 3 and 4), from which good predictions can be obtained for the total pressures at other temperatures in the range 10° to 60° C.

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The total heats of vaporization at the temperatures 25°, 40°, and 60° C were calculated for all the samples by the method of reference 5 and are presented in table II. This method is applicable to solutions as well as pure compounds, according to reference 5. Slope values were calculated from the data of table I by the method of least squares. Calculated average molecular weights were used to convert the heats of vaporization of the acids from calories per mole to calories per gram. The differences in heat of vaporization values among samples of different composition at the same temperature were found to be small.

Vapor pressures of 111.2, 118, 127.4, 139, and 152 millimeters of mercury have been reported for anhydrous nitric acids containing 10, 12, 14, 16, and 18 weight percent NO_2, respectively, at 25° C (ref. 6). These data correspond to vapor pressures of 103, 109, 120, 138, and 155 millimeters of mercury for the same compositions, respectively, obtained by extrapolation of the isobars of figure 4(a) to zero weight percent water.

SUMMARY OF RESULTS

Total vapor pressures were measured for concentrated acid of the system nitrogen dioxide - water - nitric acid within the temperature range 10° to 60° C. Results of the investigation may be summarized as follows:

1. A straight line was obtained throughout the temperature range 10° to 60° C for the logarithmic plot of vapor pressure of the acid against vapor pressure of water at equal temperature.

2. For constant nitrogen dioxide content in the range of composition studied, an increase in water content resulted in an increased total pressure.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 3, 1953

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REFERENCES

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TABLE I. - VAPOR PRESSURES OF VARIOUS NITRIC ACID, NITROGEN DIOXIDE, AND WATER MIXTURES

[Ullage, 0.456; all temperatures in °C; all pressures in mm Hg]

Sample	Analysis of stock solution				Total vapor pressure, mm Hg											
					Run 1						Run 2					
	HNO_3, percent	NO_2, percent	H_2O, percent													
1	88.42	7.82	3.76	Temperature	10.0	17.0	28.8	34.9	55.8	61.9	14.6	23.2	30.8	39.9	49.9	60.0
				Vapor pressure	46.1	67.5	130.9	181.9	517.2	691.1	59.6	99.9	149.8	245.0	397.6	641.0
2	86.27	7.60	6.13	Temperature	14.9	18.4	34.6	45.1	50.5	59.6	17.8	26.7	37.2	46.5	58.2	-----
				Vapor pressure	59.5	74.1	187.5	324.0	423.3	652.8	76.0	122.8	218.7	347.8	604.5	-----
3	83.19	7.71	9.10	Temperature	10.2	26.2	32.2	37.5	48.3	60.0	17.8	27.0	35.7	43.6	52.4	58.9
				Vapor pressure	51.8	133.1	187.2	244.4	422.2	733.0	79.7	136.2	219.2	331.1	512.2	693.2
4	86.21	10.40	3.39	Temperature	11.1	22.8	31.2	39.1	47.9	55.7	10.4	16.4	27.0	37.0	42.8	56.9
				Vapor pressure	57.6	111.7	176.2	268.5	417.2	603.3	56.5	77.6	141.0	241.4	323.7	635.7
5	84.89	10.36	4.76	Temperature	10.4	15.5	23.9	32.0	41.0	54.3	13.9	20.5	30.7	40.2	49.1	56.3
				Vapor pressure	63.3	82.0	126.8	195.7	308.1	585.1	72.7	102.9	176.5	292.2	456.8	646.7
6	82.05	10.11	7.84	Temperature	16.5	24.0	34.6	44.0	53.4	-----	10.3	14.5	20.8	30.1	48.0	54.3
				Vapor pressure	100.5	148.8	260.6	411.2	638.3	-----	87.2	85.4	121.0	200.7	513.1	648.4
7	79.78	10.35	9.87	Temperature	10.4	15.9	24.2	31.2	42.2	52.0	12.8	18.4	26.1	32.0	40.1	52.0
				Vapor pressure	78.9	105.1	167.6	246.7	427.2	679.0	87.8	122.1	187.8	256.6	390.6	679.8
8	84.64	13.40	1.96	Temperature	11.1	17.0	25.0	35.0	45.3	52.2	14.4	20.0	30.0	39.9	47.0	56.3
				Vapor pressure	66.7	91.3	141.8	240.8	402.9	564.9	78.0	105.7	182.0	303.1	432.0	677.0
9	81.35	13.58	5.07	Temperature	10.9	16.6	30.1	40.1	47.9	52.4	12.8	22.0	29.0	37.0	45.0	53.6
				Vapor pressure	75.0	105.0	218.8	369.8	542.1	668.7	84.0	143.2	207.8	318.6	473.2	712.0
10	78.50	13.35	8.15	Temperature	10.7	22.7	30.2	39.3	48.0	50.6	11.3	14.5	19.5	26.3	35.1	47.8
				Vapor pressure	94.3	179.1	267.2	421.8	574.0	711.4	99.0	118.8	154.2	223.9	351.6	639.0
11	81.42	16.79	1.79	Temperature	11.3	15.0	23.0	30.3	40.4	52.0	14.0	21.8	27.0	39.9	45.0	50.1
				Vapor pressure	85.0	103.7	157.8	228.7	382.0	674.5	91.5	148.6	196.3	378.7	490.0	598.8
12	77.58	16.75	5.67	Temperature	11.0	13.3	18.7	25.3	33.0	47.8	10.8	12.8	16.8	28.3	38.4	45.0
				Vapor pressure	110.0	123.8	161.6	230.6	346.8	681.0	110.3	121.0	153.4	273.5	448.0	614.0
13	73.99	16.66	9.35	Temperature	12.3	16.6	22.7	30.1	38.3	43.7	11.7	18.2	25.5	32.0	36.0	42.1
				Vapor pressure	151.6	186.2	254.8	366.5	534.5	681.3	144.0	203.1	288.3	394.6	474.6	627.3
14	78.27	19.37	2.36	Temperature	10.9	15.8	24.1	31.1	41.0	49.0	10.8	14.1	27.2	36.1	45.0	49.9
				Vapor pressure	90.4	117.0	185.9	268.5	445.4	657.3	89.3	106.6	216.8	347.5	540.9	690.8
15	75.37	19.28	5.35	Temperature	11.3	16.0	22.1	30.0	37.0	45.4	12.0	16.7	20.6	27.4	34.0	45.0
				Vapor pressure	132.9	167.3	225.0	334.8	468.0	691.0	139.0	175.1	211.0	285.0	405.6	617.5
16	71.76	19.27	8.97	Temperature	10.3	14.8	20.6	28.2	38.2	41.2	12.3	18.0	24.0	28.7	34.0	40.0
				Vapor pressure	151.0	190.3	257.0	374.5	546.7	690.0	162.7	218.1	299.8	379.0	487.5	647.1

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TABLE II. - CALCULATED HEATS OF VAPORIZATION OF VARIOUS NITRIC ACID, NITROGEN DIOXIDE, AND WATER MIXTURES

Sample	Analysis of stock solution, percent			Total heat of vaporization, g-cal/g (15° C), at -		
	HNO_3	NO_2	H_2O	25° C	40° C	60° C
1	88.42	7.82	3.76	164.8	162.5	159.4
2	86.27	7.60	6.13	167.9	165.5	162.4
3	83.19	7.71	9.10	172.7	170.3	167.1
4	86.21	10.40	3.39	168.4	166.0	162.9
5	84.89	10.36	4.75	162.0	159.7	156.7
6	82.05	10.11	7.84	166.8	164.4	161.3
7	79.78	10.35	9.87	171.7	169.3	166.1
8	84.64	13.40	1.96	164.9	162.5	159.5
9	81.35	13.58	5.07	169.6	167.2	164.1
10	78.50	13.35	8.15	165.0	162.7	159.6
11	81.42	16.79	1.79	159.8	157.5	154.5
12	77.58	16.75	5.67	159.6	157.4	154.4
13	73.99	16.66	9.35	157.4	155.1	152.2
14	78.27	19.37	2.36	166.1	163.7	160.6
15	75.37	19.28	5.35	159.3	157.1	154.1
16	71.76	19.27	8.97	159.6	157.3	154.4

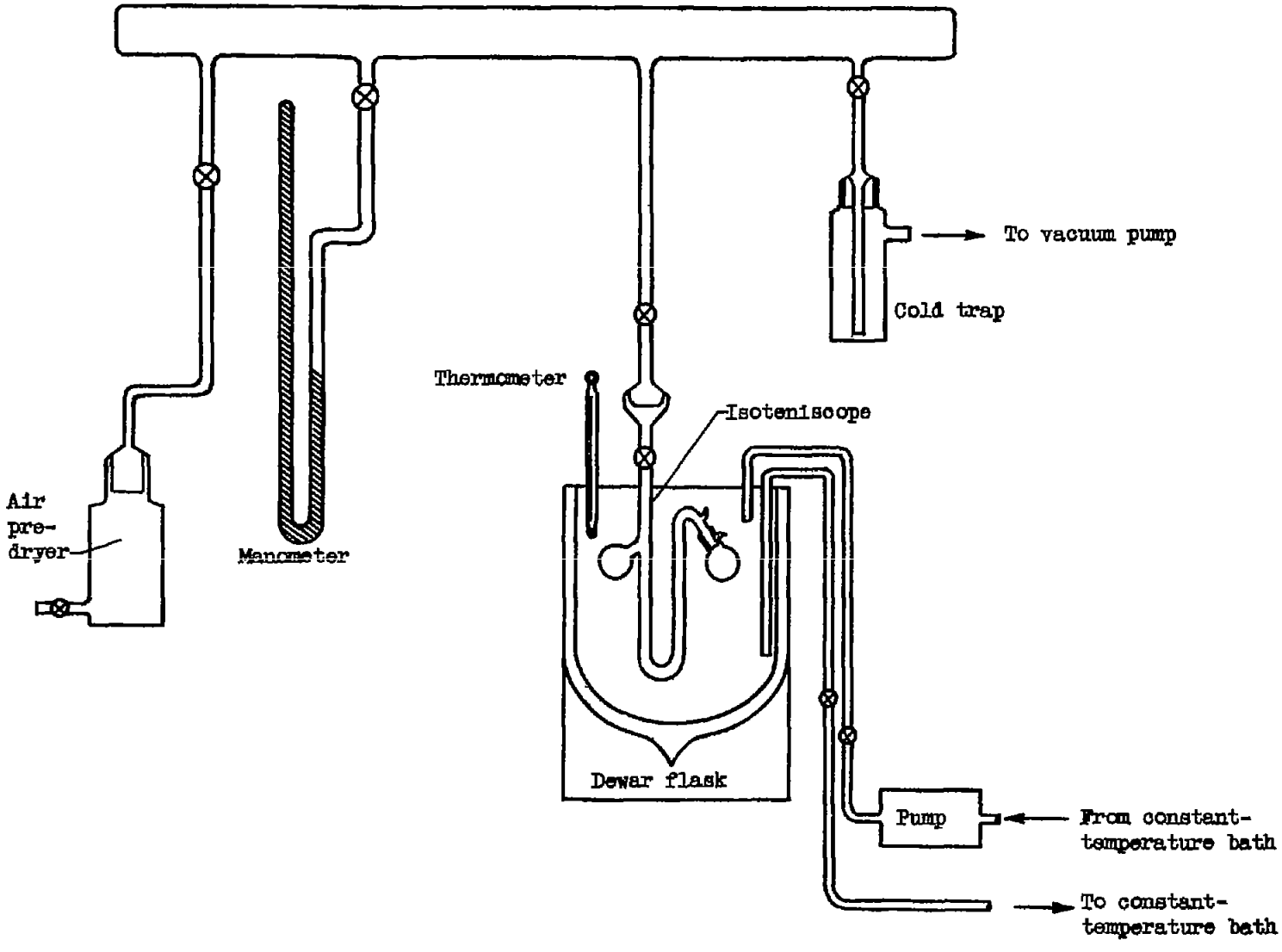

Figure 1. - Schematic diagram of vapor pressure apparatus.

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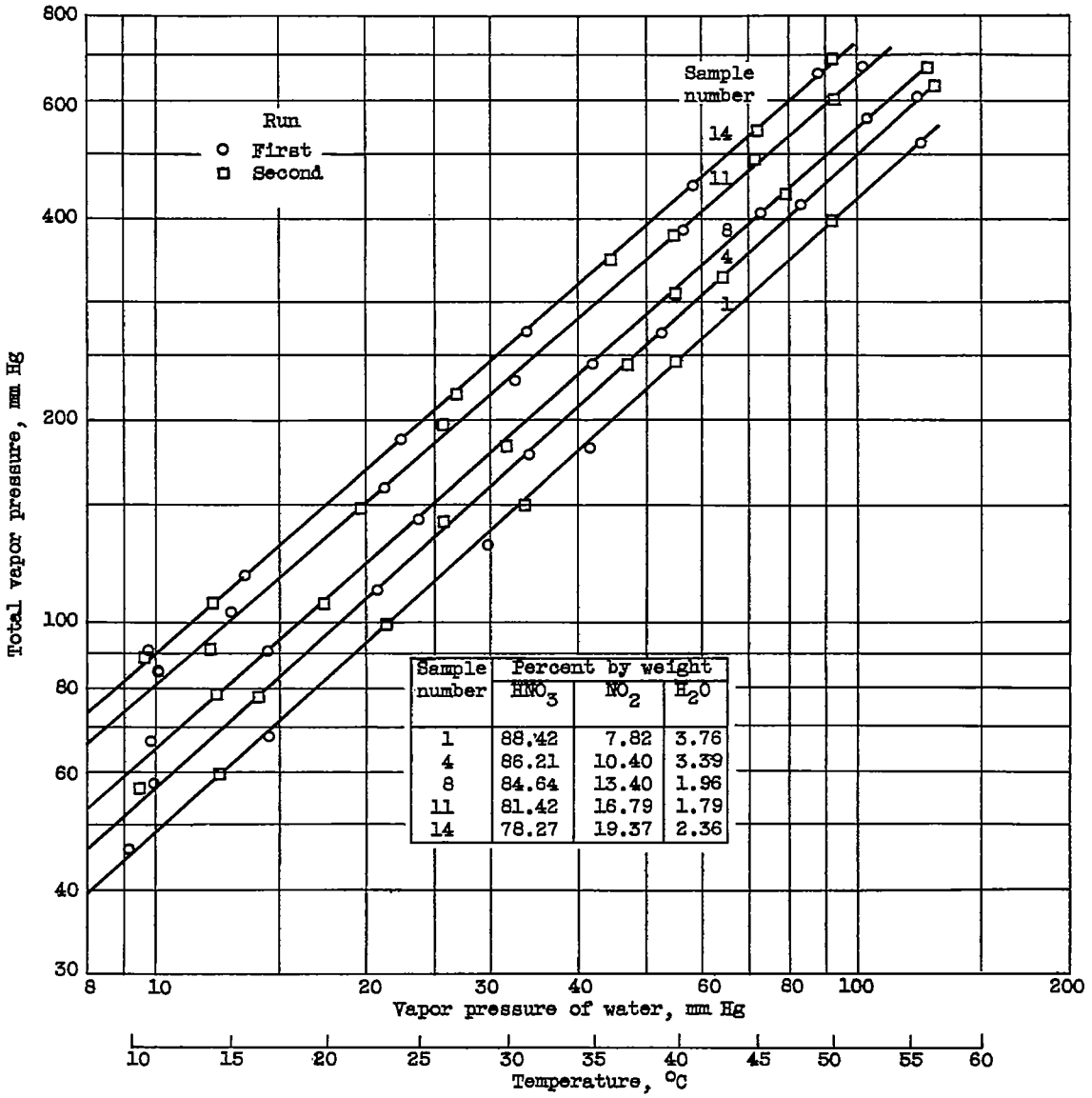
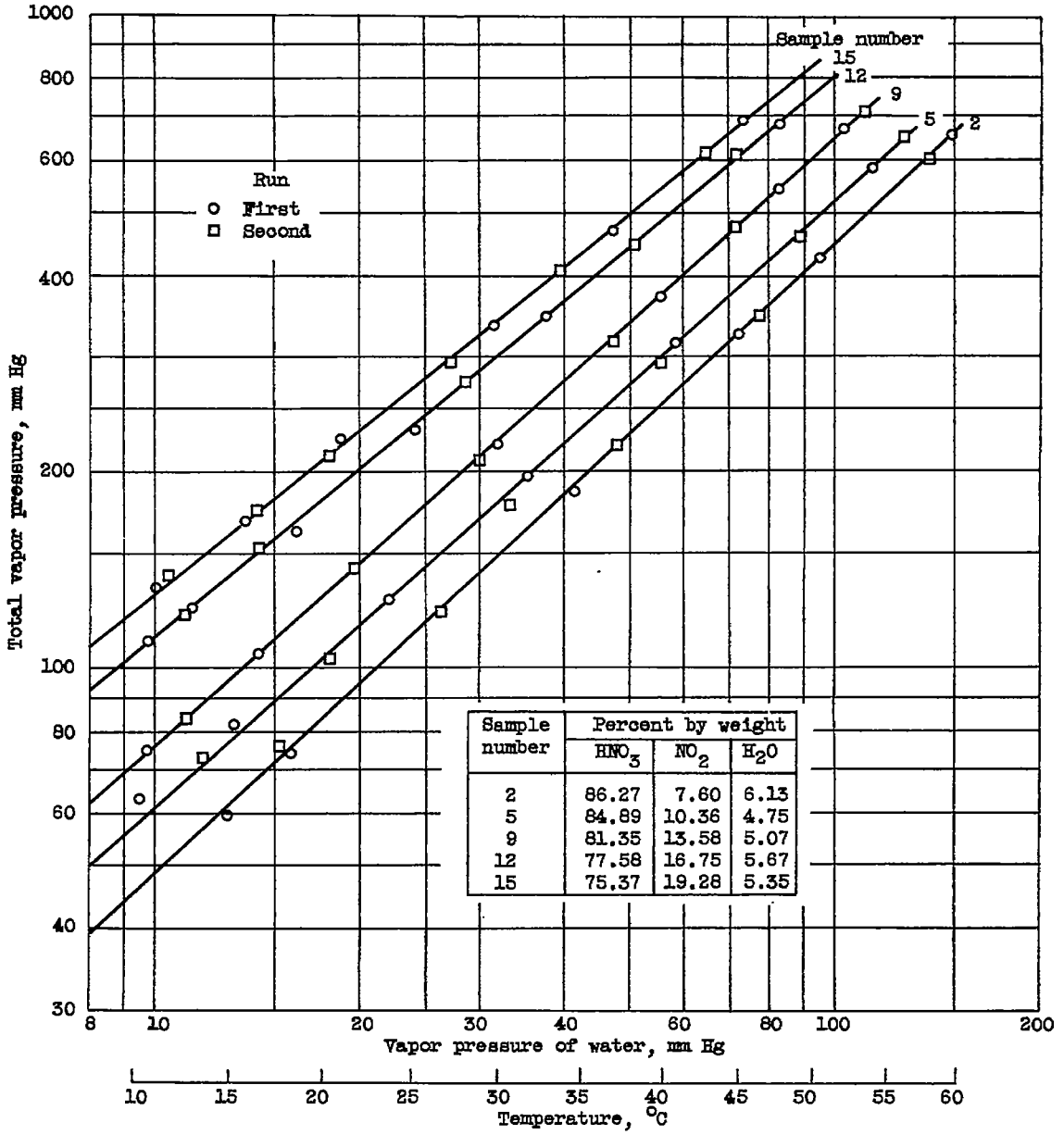


Sample number	Percent by weight		
	HNO_3	NO_2	H_2O
1	88.42	7.82	3.76
4	86.21	10.40	3.39
8	84.64	13.40	1.96
11	81.42	16.79	1.79
14	78.27	19.37	2.36

(a) Sample numbers 1, 4, 8, 11, and 14.

Figure 2. - Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.46.



Sample number	Percent by weight		
	HNO_3	NO_2	H_2O
2	86.27	7.60	6.13
5	84.89	10.36	4.75
9	81.35	13.58	5.07
12	77.58	16.75	5.67
15	75.37	19.28	5.35

(b) Sample numbers 2, 5, 9, 12, and 15.

Figure 2. - Continued. Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.46.

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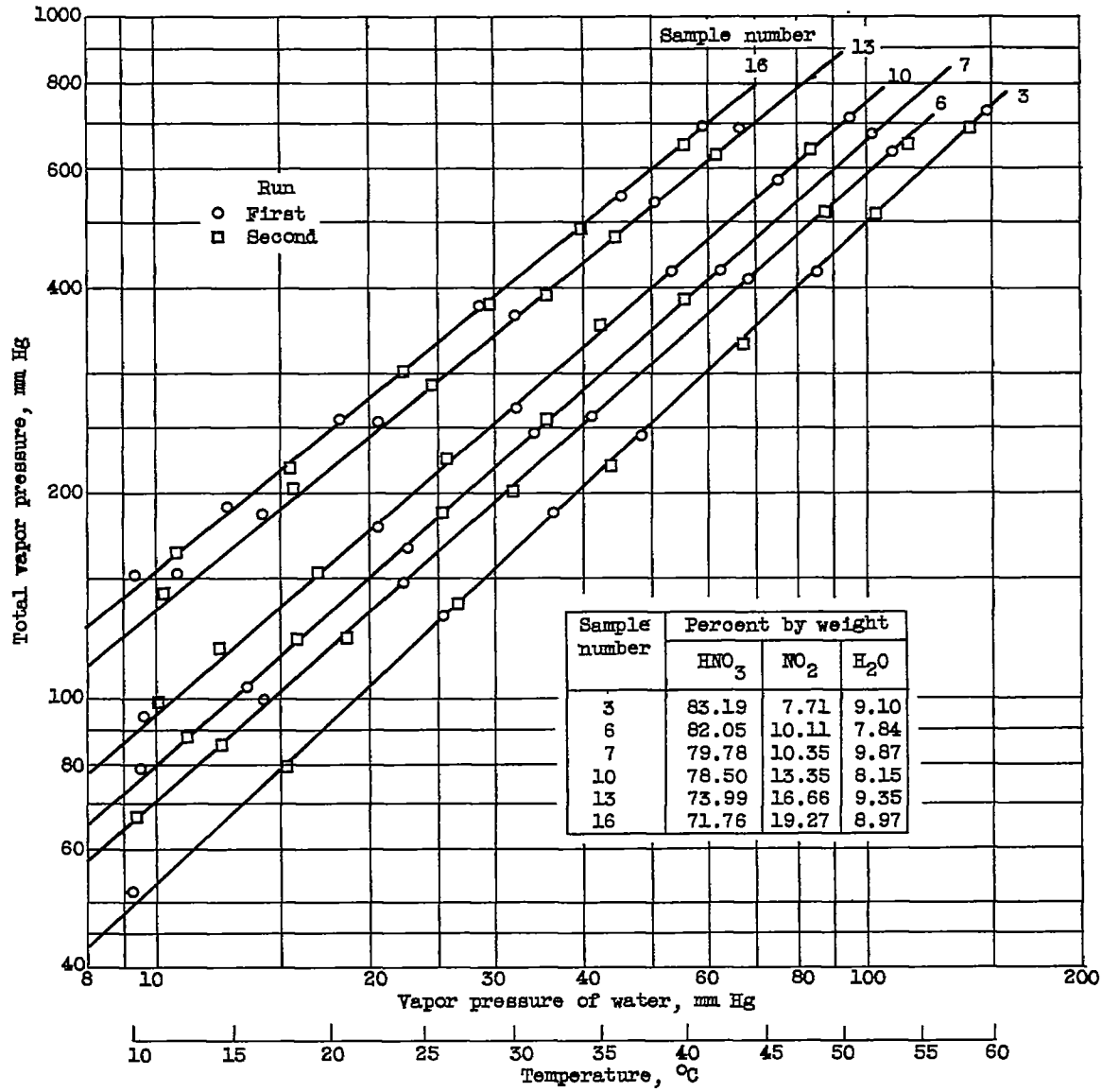

Sample number	Percent by weight		
	HNO_3	NO_2	H_2O
3	83.19	7.71	9.10
6	82.05	10.11	7.84
7	79.78	10.35	9.87
10	78.50	13.35	8.15
13	73.99	16.66	9.35
16	71.76	19.27	8.97

(c) Sample numbers 3, 6, 7, 10, 13, and 16.

Figure 2. - Concluded. Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.46.

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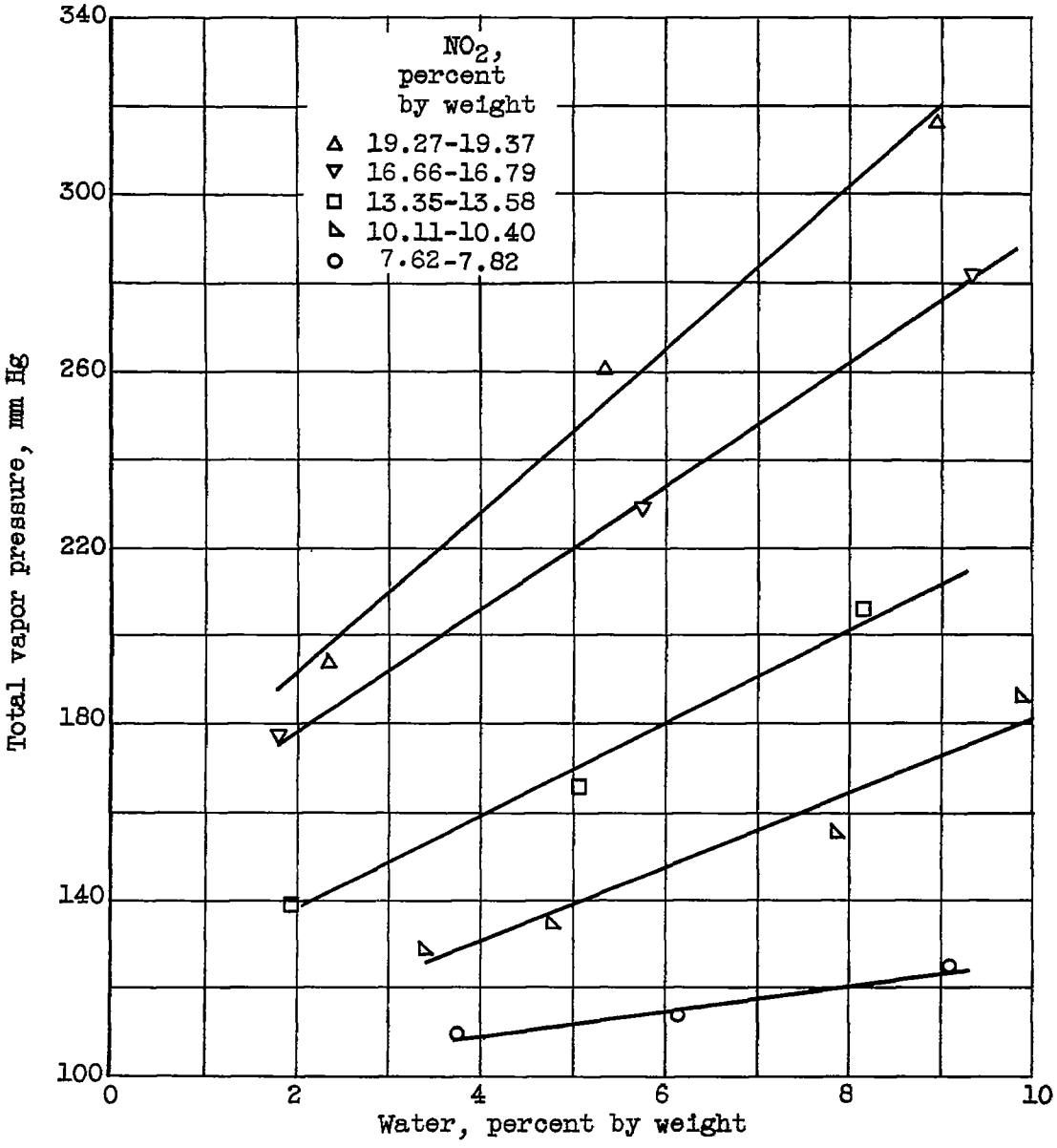

(a) Temperature, 25° C.

Figure 3. - Variation of total vapor pressure of nitric acid solutions with composition. Ullage, 0.46.

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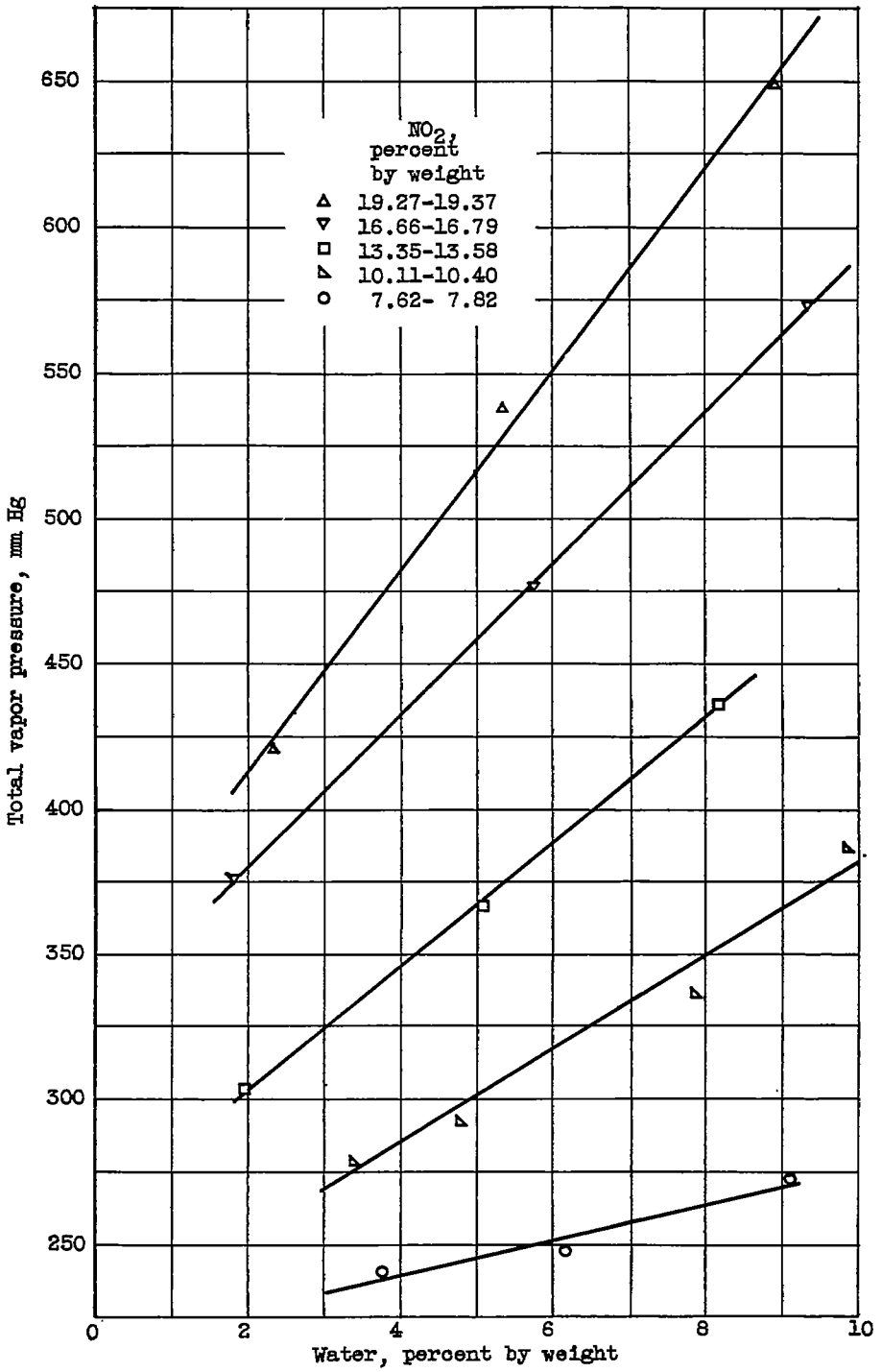
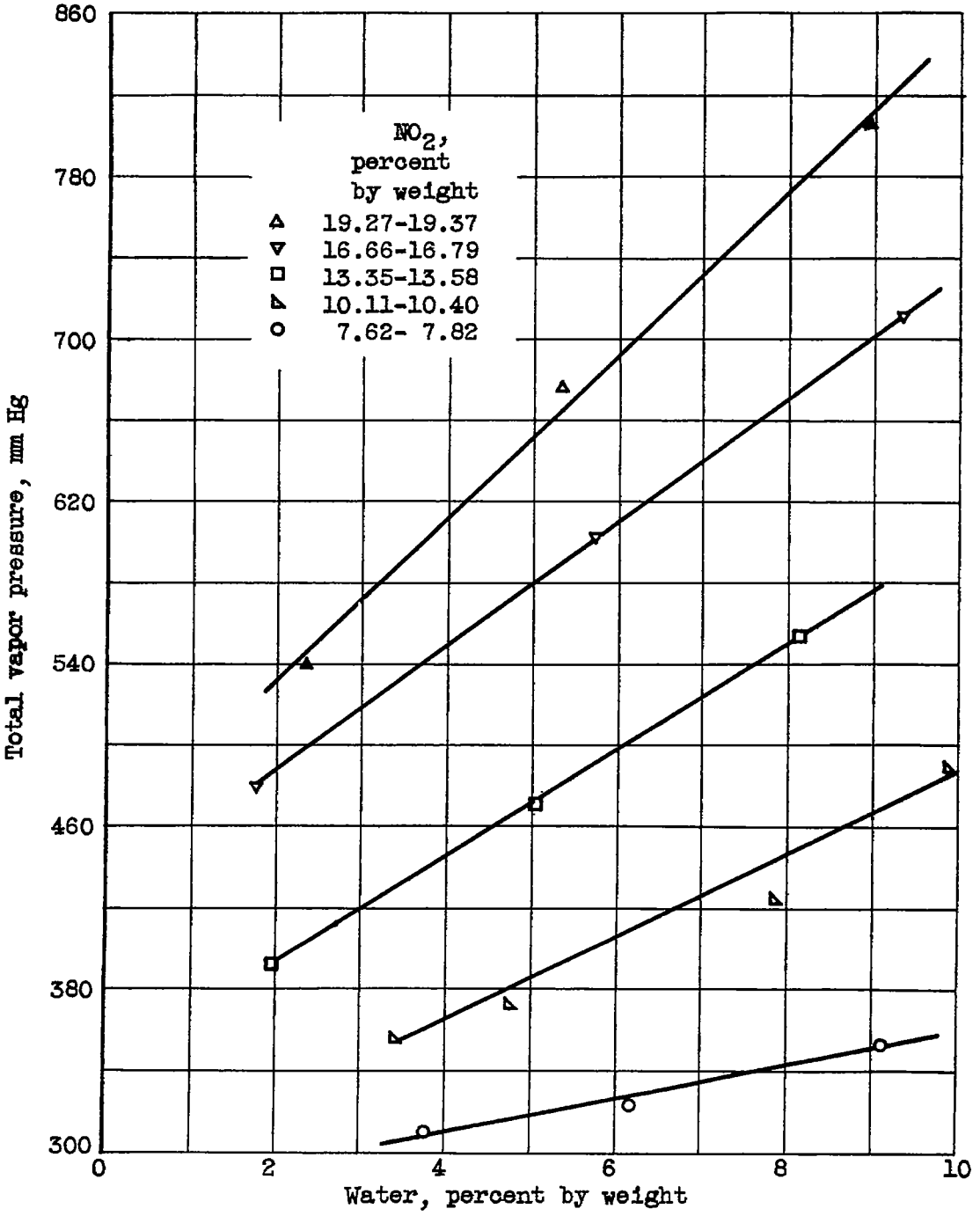


(b) Temperature, 40° C.

Figure 3. - Continued. Variation of total vapor pressure of nitric acid with composition. Ullage, 0.46.



(c) Temperature, 45° C.

Figure 3. - Concluded. Variation of total vapor pressure of nitric acid with composition. Ullage, 0.46.

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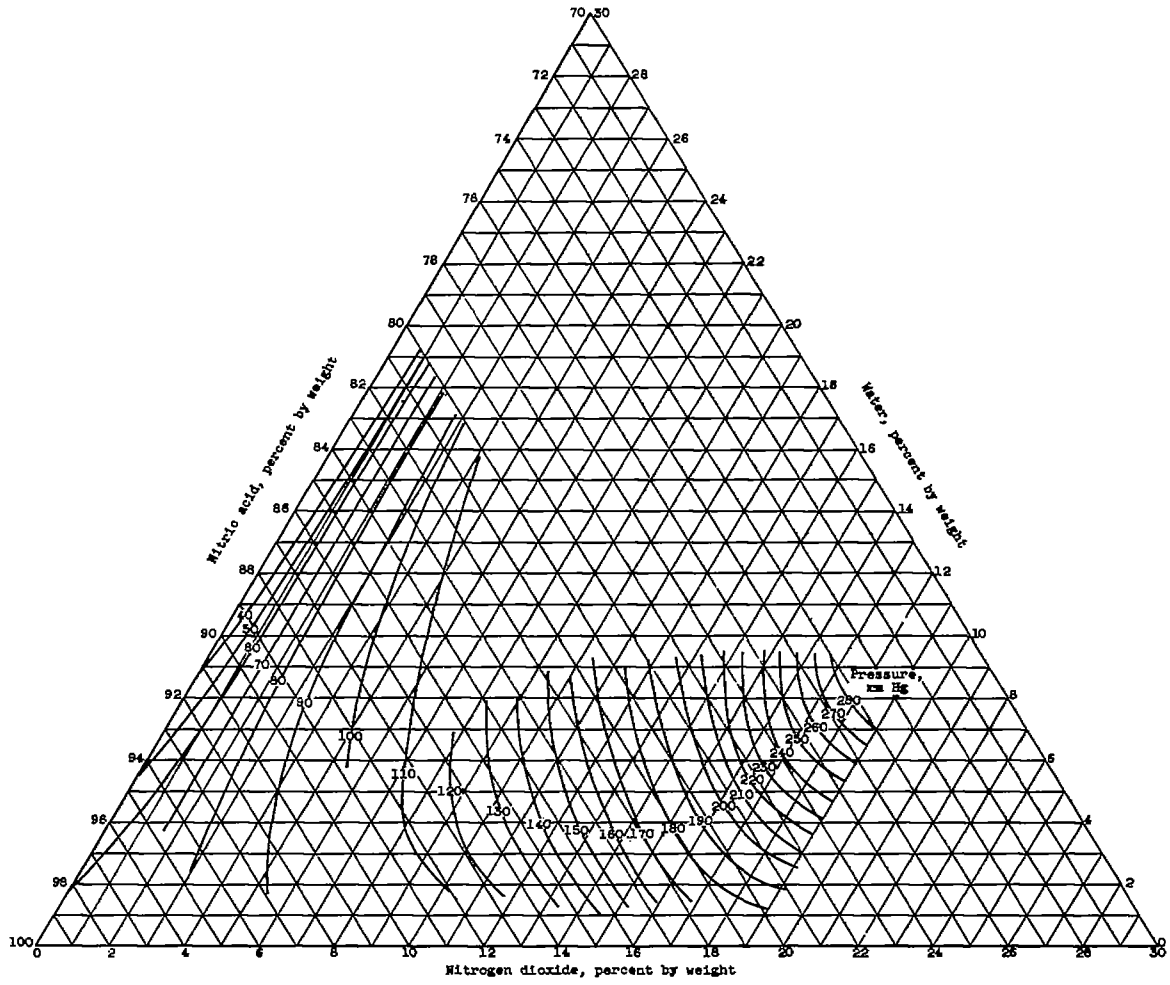
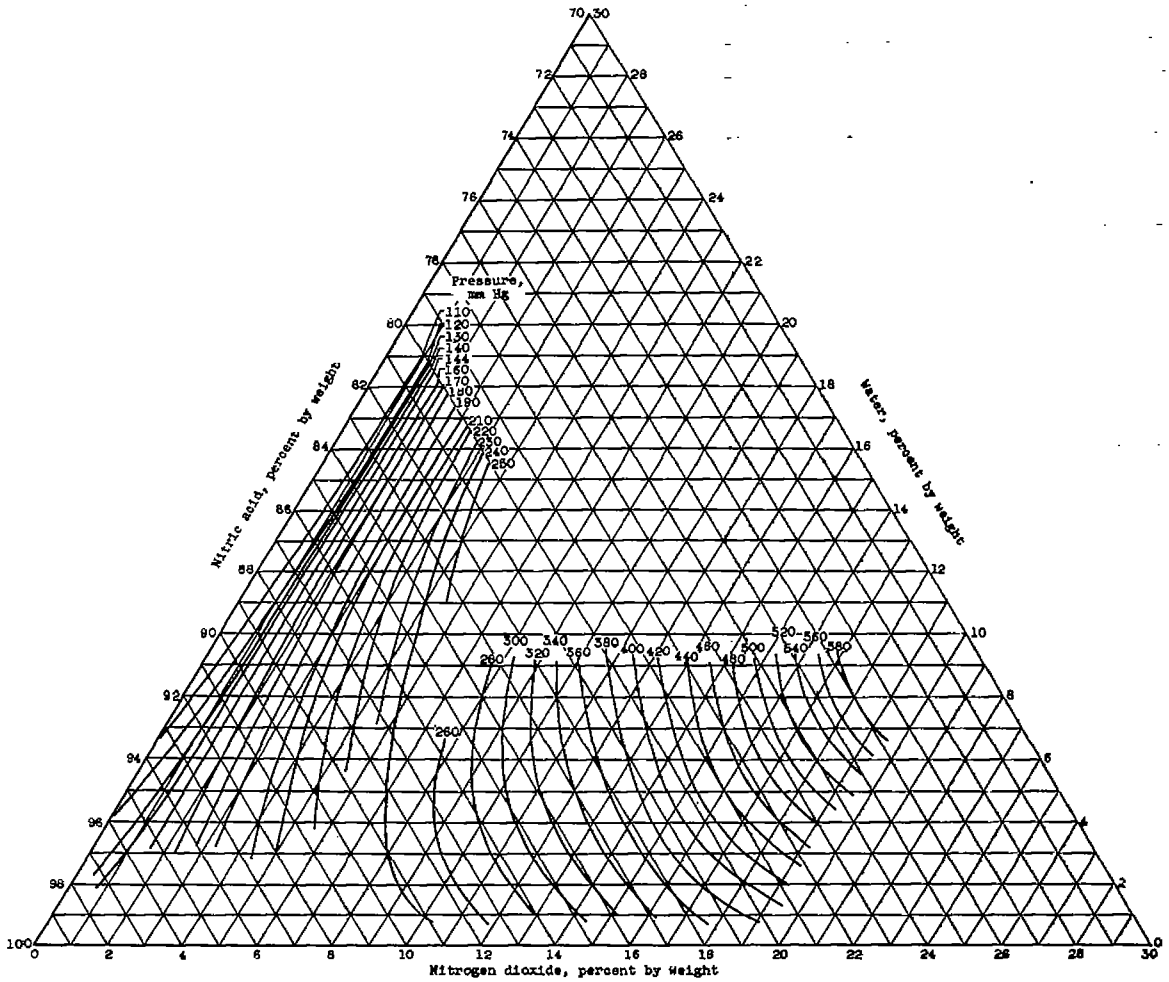


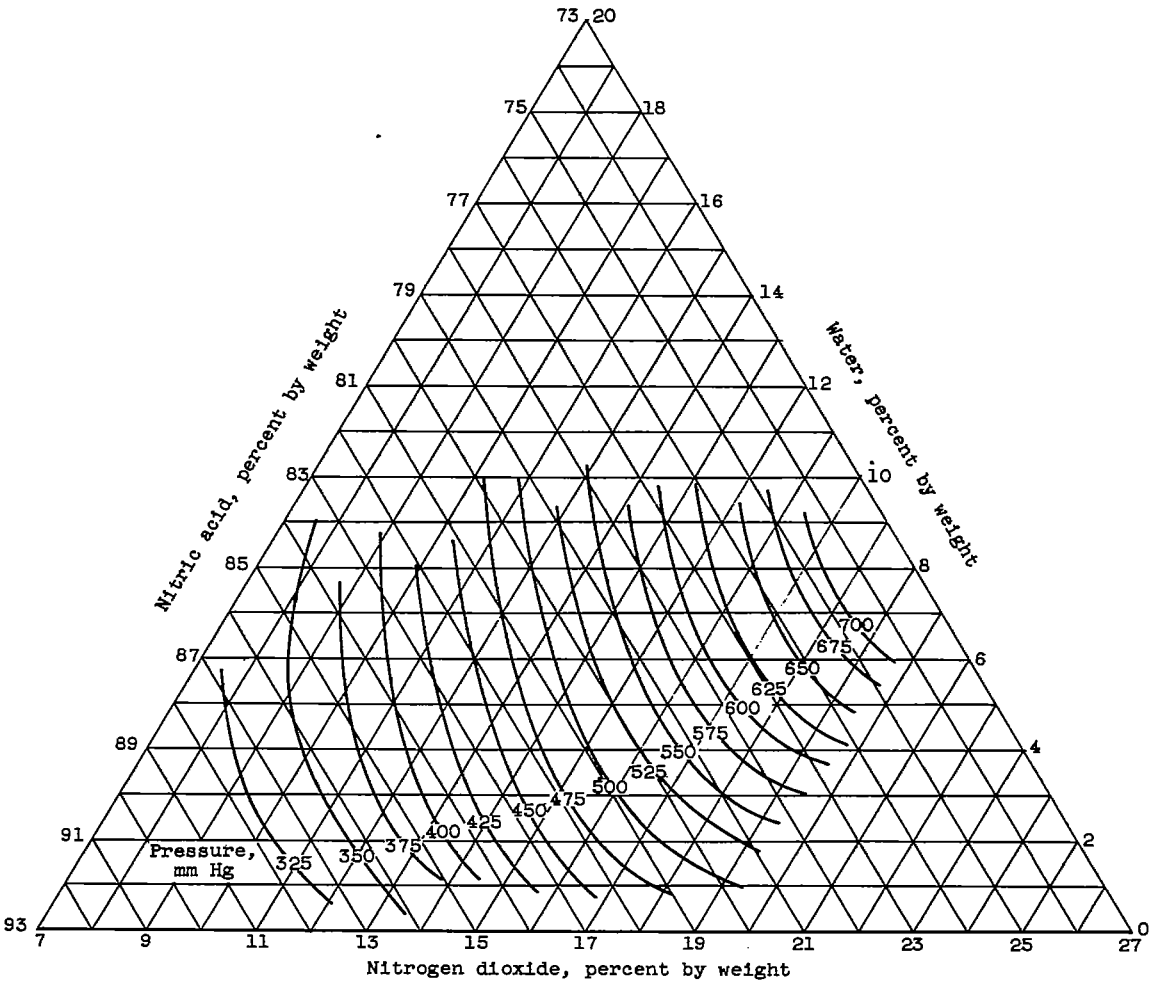
(a) Temperature, 25° C; ullage for data at pressures below 110 millimeters of mercury, 0.65.

Figure 4. - Total vapor pressures of the system, nitric acid, nitrogen dioxide, and water. Ullage, 0.46.



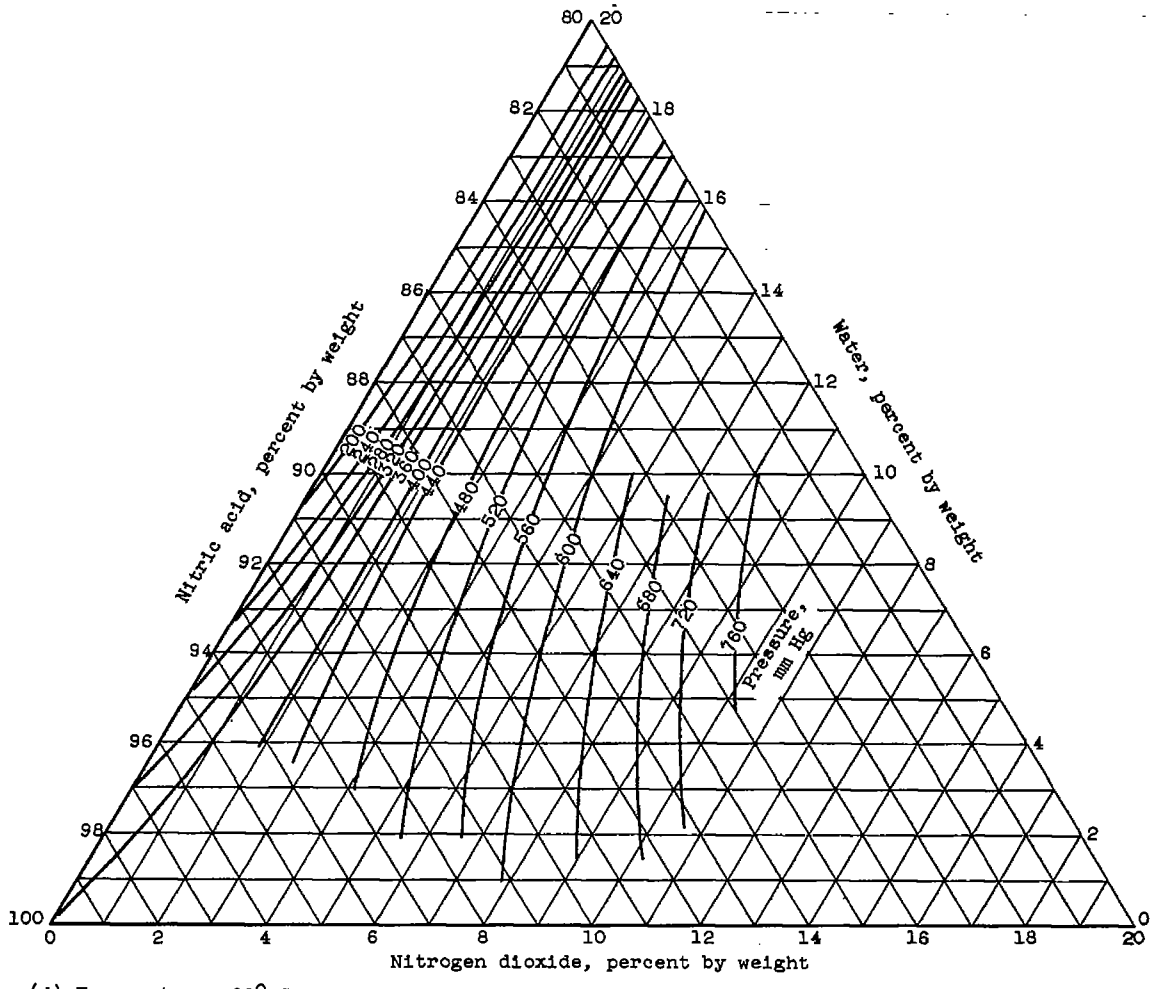
(b) Temperature, 40° C. Ullage for data at pressures below 240 millimeters of mercury, 0.65.

Figure 4. - Continued. Total vapor pressures of the system, nitric acid, nitrogen dioxide, and water. Ullage, 0.46.



(c) Temperature, 45° C.

Figure 4. - Continued. Total vapor pressures of the system, nitric acid, nitrogen dioxide, and water. Ullage, 0.46.



(d) Temperature, 60° C. Ullage for data at pressures below 600 millimeters of mercury, 0.65.

Figure 4. - Concluded. Total vapor pressures of the system, nitric acid, nitrogen dioxide, and water. Ullage, 0.46.